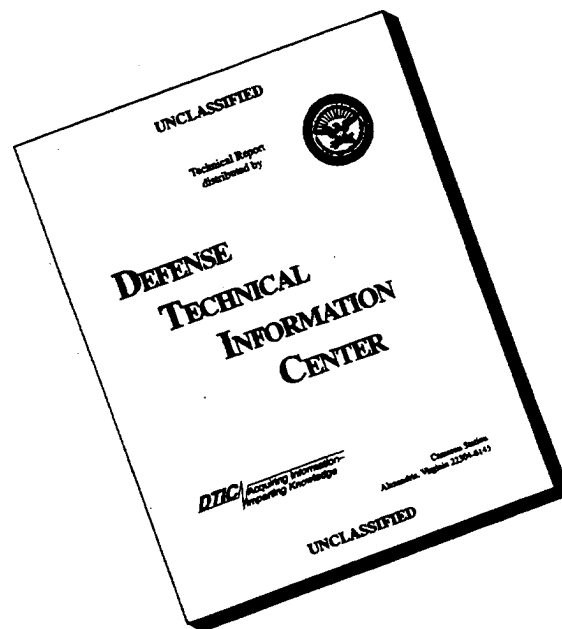


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AND CURRENT AT MICRODISK ELECTRODES.

by

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## MAGNETIC FIELD CONTROL OF THE POTENTIAL DISTRIBUTION AND CURRENT AT MICRODISK ELECTRODES.

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**Abstract.** Au and Pt microdisk electrodes (6.4, 12.5, and 25  $\mu\text{m}$  radii) have been used to investigate the influence of a uniform external magnetic field on faradaic reactions. Magnetohydrodynamic flow within a microscopic volume element adjacent to the microdisk surface results in an increase in steady-state limiting voltammetric currents for reduction and oxidation of both neutral and ionic electroactive molecules. The dependence of limiting currents on external field strength suggests the existence of a threshold value of the magnetic force necessary to induce convective flow. Above this threshold value, the voltammetric current is found to increase in proportion both to the external magnetic field strength and to the steady-state current measured in the absence of the field. The results are used to establish an empirical correlation between faradaic currents and the magnetic force acting on the solution within the depletion layer.

In low ionic strength solutions, the external magnetic field also reduces the electrostatic driving force for electron-transfer. This magnetic field-induced reaction overpotential is shown to result from a steady-state displacement of charge-balancing counterions at the electrode/solution interface, analogous to that recently observed for a rotating microdisk electrode.

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**Introduction.** We report new phenomena associated with the influence of a uniform magnetic field on molecular transport and the electric potential distribution at electrochemical interfaces. It is established that an externally applied magnetic field can alter mass-transport rates in electrochemical cells, a consequence of the magnetic force inducing convective solution flow [1-22]. The magnetic force in an electrochemical cell arises from the flux of ionic species through the magnetic field, and is given by:

$$F^V_{\text{mag}} = J \times B \quad (1)$$

In eq. (1),  $F^V_{\text{mag}}$  is the force per unit volume of solution,  $J$  is the flux of charge (coul/m<sup>2</sup>s) associated with molecular transport, and  $B$  is the magnetic field (Tesla). In a recent report from this laboratory [23, 24], we demonstrated that magnetic fields ( $\leq 1.0$  Tesla) can result in significant enhancements ( $\sim 100\%$ ) in voltammetric currents measured at Au and Pt microdisk electrodes ( $\sim 6.4$  to  $25 \mu\text{m}$  radii) for the reduction of neutral organic molecules. These preliminary results suggest that  $F^V_{\text{mag}}$  within the depletion layer surrounding a microdisk electrode is sufficiently large to induce steady-state convective mass transport.

An unusual aspect of magnetic field effects at microdisk electrodes is the dependence of  $F^V_{\text{mag}}$  on the electrode size. Because of the small size of a microdisk, the diffusive flux of an electroactive reactant increases in proportion to the inverse of the electrode radius,  $r_0$ . Consequently, significantly larger fluxes can be obtained at microdisk electrodes than at electrodes of conventional dimensions. For instance, the steady-state diffusive flux at a  $1 \mu\text{m}$ -radius disk is equivalent to that at a macroscopic disk electrode rotated at an angular velocity of  $4000 \text{ rad/s}$ . In corresponding fashion, the magnitude of the charge flux at a microdisk, i.e., current density,  $J = |J|$ , also increases as  $r_0^{-1}$ .

Using the expression for the limiting current at a microdisk [25], eq. (2),

$$i_{\text{lim}} = 4nFDCr_0 \quad (2)$$

the current density at the electrode surface,  $J_{\text{surf}}$ , can be expressed in terms of the electrode radius ( $r_0$ ), diffusivity ( $D$ ) and bulk concentration ( $C$ ) of the electroactive species.

$$J_{\text{surf}} = (4DC/\pi r_0)n \quad (3)$$

In eq. (3),  $\mathbf{n}$  is the unit surface normal, which is parallel to the flux at the surface. Combining eqs. (1) and (3) indicates that  $F^V_{\text{mag}}$  acting on the solution directly at the electrode surface, eq. (4), will increase without bound as the electrode size is decreased. In

$$F^V_{\text{mag}} = (4DC/\pi r_0)(\mathbf{n} \times \mathbf{B}) \quad (4)$$

contrast, for a fixed solution composition and field strength,  $J_{\text{surf}}$  and  $F^V_{\text{mag}}$  are essentially independent of electrode size at macroscopic electrodes, and significantly smaller than the corresponding quantities at electrodes of micrometer and submicrometer dimensions.

In the current investigation, we have explored several aspects of magnetic field effects at microdisk electrodes. First, we have quantitatively compared the enhancement in faradaic currents at a microdisk that results from a uniform magnetic field to the enhancement in current that results from forced convection at a rotating microdisk electrode (RMDE). We observe that a magnetic field of  $\sim 1\text{T}$  results in an enhanced mass transport rate that is equivalent to rotating the electrode at an angular velocity  $\sim 60\text{ rad/s}$ . The enhancement in mass-transfer rate due to the magnetic field is 100 to 1000 times larger than that previously reported for conventional size electrodes [1-13]. Second, based on measurements employing both charged and neutral redox-active molecules, we report preliminary evidence of a threshold value of  $F^V_{\text{mag}}$  necessary to induce fluid convection at the microelectrode surface. Above this critical value, we show that the enhancement in mass-transport rates increases linearly in relation to the product of the current in the absence of the magnetic field and the magnetic field strength. This latter result suggests that convective mass transport rates at a microelectrode are proportional to the magnetic force,  $F^V_{\text{mag}}$ , acting on the depletion layer.

A third aspect of the current report concerns the effect of the magnetic field on the steady-state distribution of ions and electric potential at the electrode/solution interface. A well known advantage of using microdisks in electrochemical investigations is the ability to perform quantitative measurements in low ionic strength solutions [26, 27]. This experimental capability results from the increased interfacial concentration of supporting electrolyte counterions in response to the electric field created by the electrogeneration of charged products. Recently, we demonstrated that the depletion layer ion and potential

distribution may be disrupted by rotation of the microdisk electrode [28]. For instance, in low ionic strength solutions, voltammetric currents corresponding to the oxidation or reduction of a neutral species, e.g., ferrocene, were found to *decrease* with increasing rotation rate. The physical reason for this anomalous behavior, which is specific to neutral electroactive species, is that the charge compensating electrolyte ions within the depletion layer are removed by convective flow more rapidly than they are replenished by migration. We now demonstrate that a similar reduction in driving force arises from magnetic-field engendered fluid convection. A significant and interesting difference in convective fluid flow induced by electrode rotation and by a magnetic field is that the latter is locally confined to the depletion layer region.

**Experimental.** Au (6.4  $\mu\text{m}$  radius) and Pt (12.5 and 25  $\mu\text{m}$  radius) microdisk electrodes were constructed by sealing a Au or Pt wire in a glass tube using a  $\text{H}_2/\text{O}_2$  flame. The end of the tube was sanded to expose a metal microdisk. Electrodes were polished with  $\text{Al}_2\text{O}_3$  (0.02  $\mu\text{m}$ ), washed with distilled water, and sonicated in distilled water for ~2 min.

A GMW Associates Model 5403 electromagnet having 7.6 cm-diameter poles separated by ~2 cm was used to apply a uniform magnetic field across the electrochemical cell (see Fig. 1). A one-compartment, three-electrode cell containing either a  $\text{Ag}/\text{Ag}_x\text{O}$  or  $\text{Ag}/\text{AgCl}$  reference electrode, a Pt wire auxiliary electrode, and a Au or Pt microdisk electrode, was used throughout the study. The microelectrode was oriented vertically in the cell, such that the surface of the electrode was parallel to the magnetic field (see Fig. 1). The angle  $\theta$  between the net current vector,  $i$  (orthogonal to the microelectrode surface), and the magnetic field,  $B$ , defines the direction of the net magnetic force acting on the solution in the vicinity of the microelectrode, i.e.,  $F_{\text{mag}}^{\text{net}} = i(l \times B)$ , where  $l$  is the unit displacement vector that points in the direction of the net current and  $i = |i|$ . For an electrochemical reduction,  $i$  and  $l$  are directed into the surface of the electrode, and  $\theta = 90^\circ$ . For oxidation reactions,  $\theta = 270^\circ$ . In either case,  $F_{\text{mag}}^{\text{net}}$  is parallel to the electrode surface. Because the current is radial convergent at a microelectrode for a reduction reaction (and radial divergent for oxidation), the local magnetic force in the solution is a function of position. This point is discussed below in more detail.

The magnetic field strength was varied between 0 and 0.8 Tesla (T) by adjusting the current to the electromagnet. Field strengths were measured using a gauss meter (F. W. Bell,

Model 4048) placed close to the surface of working microelectrode. A commercial rotating disk apparatus (Pine Instrument Co., Model No. PIR) was used to rotate the microelectrode at angular velocities ( $\omega$ ) between 0 to 252 rad/s. Voltammograms were recorded using a Princeton Applied Research Corp. Model 173 potentiostat, Model 175 programmer, and a Kipp & Zonen BP 90 x-y-t recorder.

Tetra(n-butyl)ammonium hexafluorophosphate (TBAPF<sub>6</sub>; Sigma) was recrystallized in absolute ethanol and dried under vacuum. Nitrobenzene (NB; Aldrich 99+%) was stored over molecular sieves. All other chemicals (acetonitrile (CH<sub>3</sub>CN; Fisher Scientific, HPLC grade), acetophenone (AP; EM Science, 98+%), benzophenone (BP; Janssen Chimica, 99%), potassium ferrocyanide (K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O; Mallinckrodt), potassium ferricyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>; Mallinckrodt), potassium chloride (KCl; Mallinckrodt)) were analytical reagent grade and used as received. Aqueous solutions were prepared using water from a Barnstead "E-pure" purification system (18 M $\Omega$ -cm resistivity).

## Results and Discussion.

*Comparison of the Voltammetric Responses of a Stationary Microdisk Electrode in a Magnetic Field and a Rotating Microdisk Electrode.* Fig. 2 shows the voltammetric behavior of a 25  $\mu$ m-radius Pt electrode in CH<sub>3</sub>CN solutions containing 1 M nitrobenzene (NB). The sigmoidal shaped voltammograms result from the 1-e<sup>-</sup> reduction of NB to the corresponding radical anion.



The voltammetric curves shown in Fig. 2 correspond to solutions containing either 0.1 M or 0.01 M TBAPF<sub>6</sub> as the supporting electrolyte. In the absence of an applied magnetic field ( $B = 0$ ), the shape of the voltammetric wave in either solution is consistent with diffusional transport of reactant to the microdisk surface. The limiting current,  $i_{lim}$ , measured in the 0.01 M TBAPF<sub>6</sub> solution is ~15% larger than in the 0.1 M TBAPF<sub>6</sub> solution, a difference that reflects the viscosities of these solutions. Values of  $i_{lim}$  at the 25  $\mu$ m-radius disk yield molecular diffusivities (eq. (2)) for NB of  $1.8 \times 10^{-5}$  and  $2.1 \times 10^{-5}$  cm<sup>2</sup>/s in the 0.1 and 0.01 M TBAPF<sub>6</sub> solutions, respectively.



Qualitatively similar voltammetric responses are obtained using either 6.4  $\mu\text{m}$ -radius Au and 12.5  $\mu\text{m}$ -radius Pt microdisks for solutions containing NB at concentrations ranging from 0.001 M to 9.1 M (note: 9.1 M NB corresponds to solutions containing only NB and supporting electrolyte; i.e., no solvent is present in the solution) [29, 30]. However,  $i_{\text{lim}}$  exhibits a highly nonlinear dependence on NB concentration, obtaining a maximum value in solutions containing  $\sim 2.5$  M NB. For concentrations above 2.5 M,  $i_{\text{lim}}$  decreases with increasing NB concentration. This nonlinear behavior results from the dependence of molecular diffusivity on NB concentration, and has been analyzed using a redox species/solvent interdiffusion model [31].

Application of a uniform magnetic field ( $\theta = 90^\circ$ ) results in an increase in  $i_{\text{lim}}$  for NB reduction. For instance, Fig. 2 shows that  $i_{\text{lim}}$  in the 0.1 M TBAPF<sub>6</sub> solution increases from a diffusion-controlled value of  $\sim 18$   $\mu\text{A}$  to  $\sim 40$   $\mu\text{A}$  at a field strength of 0.8 T. A slightly smaller increase is observed in the 0.01 M TBAPF<sub>6</sub> solution. Similar to the nonlinear dependence of  $i_{\text{lim}}$  on NB concentration in the absence of a field, we observe that the magnetic-field enhancement of  $i_{\text{lim}}$  also exhibits a maximum value at intermediate redox concentrations ( $\sim 2.5$  M NB), and becomes negligibly small at either very low (1 mM) or very high (9.1 M) NB concentrations. A more detailed analysis of the magnetic field enhancement of  $i_{\text{lim}}$  is discussed in a later section.

The shape of the voltammetric wave for NB reduction is dependent upon both the magnetic field strength and supporting electrolyte concentration. In the 0.1 M TBAPF<sub>6</sub> solution, the voltammetric waveshape is essentially independent of the field strength ( $B$ ), exhibiting only a small shift ( $\sim 100$  mV) in half-wave potential,  $E_{1/2}$ , with increasing  $B$ . In contrast, a significant reaction overpotential is observed upon decreasing the TBAPF<sub>6</sub> concentration to 0.01 M. For instance, Fig. 2 shows that  $E_{1/2}$  shifts negative by  $\sim 800$  mV when the magnetic field is increased from 0 to 0.8 T.

As discussed in the *Introduction* section, the flux of charged species through a uniform magnetic field induces convective flow at the electrode surface. Prior to describing this phenomenon in terms of the transport of specific ions, it is instructive to compare the effect of the magnetic-field induced convective flow to forced convection caused by rotation of the electrode. The voltammetric response of the 25  $\mu\text{m}$ -radius Pt disk is shown in Fig. 3 as a function of angular velocity,  $\omega$ . The rotating microdisk electrode (RMDE) measurements

were made in the same  $\text{CH}_3\text{CN}$  solutions used to record the voltammetric responses as a function of magnetic field strength. In agreement with previous RMDE experiments [28], rotation of the electrode results in an increase in  $i_{\text{lim}}$  for NB reduction, corresponding to an increase in the transport of NB to the electrode surface by forced convection. Limiting currents at the RMDE increase approximately as  $\omega^{1/2}$  (see ref. 28 for a more detailed analysis of RMDE voltammetry). However, in addition, and analogous to the magnetic field dependency, a large shift in  $E_{1/2}$  is observed at high rotation rates when the supporting electrolyte concentration is lowered from 0.1 to 0.01 M. Qualitatively, the effects of electrode rotation (Fig. 3) and a uniform magnetic field (Fig. 2) on the voltammetric response are quite similar.

The voltammetric limiting current at a RMDE is given [32, 33] by

$$\frac{i_{\text{lim}}}{A} = 0.64nFD^{2/3}\omega^{1/2}\nu^{-1/6}C_{\text{redox}}\epsilon^{1/3} \quad (6)$$

where  $\epsilon$  (the so-called eccentricity factor) is defined as the ratio of the distance between the axis of rotation and the center of the disk (R) relative to the radius of the microdisk ( $r_0$ ), i.e.,  $\epsilon = R/r_0$ . Eq. (6) is strictly applicable in the limit  $R \gg r_0$ . The eccentricity factor accounts for the dependence of the tangential fluid velocity on the radial distance  $r$  from the center of the electrode. For a rotating disk, both the angular ( $v_\phi$ ) and radial ( $v_r$ ) fluid velocities are proportional to the position,  $r$ . Thus, the rate at which the reactant is transported to the electrode surface (by tangential convective flow) will increase if the electrode is located off of the rotation axis (i.e.,  $R \neq 0$ ). Using the data in Fig. 3 for the  $\text{CH}_3\text{CN}/0.1 \text{ M TBAPF}_6$  solution, and  $D = 1.8 \times 10^{-5} \text{ cm}^2/\text{s}$  for NB, we compute  $\epsilon \sim 10$ . Thus, the Pt microdisk electrode used in these measurements is positioned  $\sim 250 \mu\text{m}$  ( $= R$ ) off of the axis of rotation.

The data in Fig. 2 and 3 indicate that the enhancement in  $i_{\text{lim}}$  ( $\sim 20 \mu\text{A}$ ) resulting from a 0.8 T magnetic field is approximately equivalent to that obtained by rotation of the electrode at  $\sim 50 \text{ rad/s}$ . Using the conventional definition of the mass-transfer coefficient [34], eq. (7),

$$m = \frac{i_{\text{lim}}}{nFA C_{\text{redox}}} \quad (7)$$

we compute that the increase in current due to a magnetic field of  $B = 0.8 \text{ T}$  corresponds to an increase in the mass-transfer coefficient ( $\Delta m$ ) of  $1.2 \times 10^{-2} \text{ cm/s}$ . For comparison,  $\Delta m$  resulting from magnetic field-induced convective flow at macroscopic electrodes is typically several orders of magnitude smaller. For example, using independent data reported by Olivier and coworkers [13] and by Kim and Fahidy [8] for the reduction of  $\text{Fe(CN)}_6^{3-}$  and  $\text{CuSO}_4$  at macroscopic electrodes (a 0.2 cm diameter Pt disk at  $B = 0.9 \text{ T}$  and a  $3 \times 3 \text{ cm}^2$  Cu plate at  $B = 0.5 \text{ T}$ , respectively), we compute field-induced enhancements in mass-transfer coefficient ranging from  $2.6 \times 10^{-5}$  to  $1.0 \times 10^{-4} \text{ cm/s}$ . We believe that the 2-3 orders of magnitude increase in  $\Delta m$  at microdisk electrodes is due to the much larger current density, and thus, magnetic force (per volume), obtainable at these electrodes. A quantitative description of the magnetic force and resulting convective flow at microelectrodes does not currently exist.

#### *Microscopic Description of the Interaction of the Magnetic Field with Molecular Fluxes.*

In proposing a mechanism of the magnetic field effects that accounts for both the enhanced limiting currents and the large  $B$ -dependent shift in  $E_{1/2}$  at low electrolyte concentrations, we first recall the basic description of the depletion layer structure at a microdisk electrode. Electroneutrality requires that the negative charge resulting from electrogeneration of  $\text{NB}^-$  be balanced by an increase and/or decrease in the concentrations of the supporting electrolyte cation and anion, respectively. Either of these processes occur by the rapid transient fluxes of electrolyte ions on the timescale of the slow scan voltammetric experiments reported in Figs. 2 and 3. In solutions containing an excess concentration of supporting electrolyte, i.e.,  $C_{\text{elec}}/C_{\text{redox}} \gg 1$  (where  $C_{\text{redox}}$  and  $C_{\text{elec}}$  are the redox and electrolyte concentrations, respectively), the concentration of  $\text{NB}^-$  is negligibly small in comparison to the concentrations of  $\text{TBA}^+$  and  $\text{PF}_6^-$ . For this limiting case, the concentrations of electrolyte ions within the depletion layer are essentially equal to their corresponding bulk solution value. However,  $C_{\text{elec}}/C_{\text{redox}} \ll 1$  for the experiments reported in Figs. 2 and 3, and the condition of excess electrolyte cannot be assumed. Specifically, mass-transport limited reduction of 1M NB requires a significant increase in the concentration of  $\text{TBA}^+$  within the depletion layer in order to maintain electroneutrality. A

concurrent decrease in the depletion layer concentration of  $\text{PF}_6^-$  must also occur. It can readily be shown that the equality

$$[\text{NB}^-] \approx [\text{TBA}^+] \quad (8)$$

is a reasonable approximation within the depletion layer when  $C_{\text{elec}}/C_{\text{redox}} \ll 1$  [35].

Based on the above description of the depletion layer structure, we propose the following general description of the influence of an external magnetic field. Of the four species comprising the solution within the depletion layer (NB;  $\text{NB}^-$ ,  $\text{CH}_3\text{CN}$ , and  $\text{TBA}^+$ ), only NB and  $\text{NB}^-$  have nonzero fluxes during the steady-state voltammetric experiments. Since NB is electrically neutral, its flux cannot contribute to the magnetic force. Thus, the electrogenerated product,  $\text{NB}^-$ , is the only species within the depletion layer that interacts directly with the magnetic field, i.e.,  $F_{\text{mag}}^V$  is due to the net flux of  $\text{NB}^-$  through the depletion layer.

The voltammetric currents in Fig. 2 reflect the transport-limited electroreduction of NB. Thus, in order to explain the magnetic field enhancement of current, it is necessary to consider how the force exerted on  $\text{NB}^-$  is coupled to the flux of NB to the electrode surface. A mechanism consistent with the experimental observations is that acceleration of  $\text{NB}^-$  by the magnetic field induces convective solution flow, a consequence of viscous drag within the depletion layer on the electrogenerated ion. To determine the direction of the magnetic force at any point in solution, and thus the direction of convective flow, we recall that electrogenerated  $\text{NB}^-$  is transported away from the microdisk surface in a quasi-radial pattern, and that the direction of positive current opposes that of the anion flux (i.e., positive current is directed inward toward the surface for this reaction). The direction of the magnetic force within any volume element in the depletion layer is then determined from eq. (1). As schematically drawn in Fig. 4, when B is parallel to the electrode surface,  $F_{\text{mag}}^V$  points from left-to-right for essentially all regions of the solution layer adjacent to the electrode. Thus, the magnetic force tends to accelerate essentially all product ions from left-to-right across the electrode surface. (This description is not exactly correct; upward and downward directed forces occur near the left and right-hand edges of the electrode, respectively, as shown in the schematic drawing). In addition, because of the radial divergence of the flux of  $\text{NB}^-$ , the current density at any point in solution is approximately inversely proportional to the

distance from the electrode. Thus,  $FV_{\text{mag}}$  for any solution element is also expected to decay rapidly as one moves from the electrode surface into the bulk solution. Consequently, the magnetic force acting on the charge carrying ions is localized to the depletion layer region adjacent to the microdisk surface.

*Origin of the Magnetic Field-Induced Overpotential.* Fig. 5 schematically depicts the ion distribution at a stationary microdisk electrode in the absence and presence of a magnetic field, and the ion distribution at a RMDE. These drawings correspond to low ionic strength solutions, and are useful in understanding the shift in  $E_{1/2}$  that occurs at microdisk electrodes in the presence of a magnetic field or when rotated. As described above, in the absence of a magnetic field or rotation, the electrochemical generation of a charged species causes the migration of charge-compensating ions to the electrode surface (Fig. 5a). Fluid convection caused either by the magnetic field (Fig. 5b) or electrode rotation (Fig. 5c) will tend to transport both the electrogenerated ion ( $NB^-$ ) and counterion ( $TBA^+$ ) out of the depletion layer region. The steady-state concentration of counterions ( $TBA^+$ ) within the depletion layer will thus depend on the rate at which they migrate from the bulk solution to the surface, relative to the rate at which they are transported away from the surface by convection.

As either  $B$  or  $\omega$  increases, the corresponding increase in convective transport will reduce the ion concentration within the depletion layer, resulting in a depletion layer that has a composition approaching that of the bulk solution. The decrease in ion concentration causes a decrease in the solution conductivity near the surface, resulting in a significant overpotential during the voltammetric experiment. The potential loss can be expressed as the difference in the electrostatic potential between the bulk of the solution ( $\phi^S$ ) and the plane of electron transfer ( $\phi^{\text{PET}}$ , where the PET corresponds roughly to the closest approach of the redox molecules to the surface [36]). For the general redox reaction,  $O + e \rightleftharpoons R$ ,

$$(E - E^\circ) - (\phi^{\text{PET}} - \phi^S) = (RT/nF) \ln(C_O/C_R) \quad (8)$$

where  $C_O$  and  $C_R$  represent the concentrations of  $O$  and  $R$  at the PET. Eq. (8) is simply the Nernst equation written to take into account the effect of the electrostatic potential at the PET on the chemical potentials of  $O$  and  $R$ . For a neutral redox species and  $C_{\text{elec}}/C_{\text{redox}} \ll 1$ , it

has been theoretically [27] and experimentally [37] demonstrated that  $(\phi^{\text{PET}} - \phi^{\text{S}})$  increases at a rate of  $RT/nF$  ( $\sim 59/n$  mV at room temperature) per decade decrease in  $C_{\text{elec}}/C_{\text{redox}}$ .

In the absence of fluid convection induced by rotation or the magnetic field, the quantity  $(\phi^{\text{PET}} - \phi^{\text{S}})$  is negligibly small, and essentially all of the applied potential is used to drive the electrode reaction. When  $\omega$  or  $B$  are finite,  $(\phi^{\text{PET}} - \phi^{\text{S}})$  may be quite large, as apparent in the large shift in  $E_{1/2}$  observed in the voltammograms recorded for NB reduction in  $\text{CH}_3\text{CN}/0.01 \text{ M TBAPF}_6$  solutions. Fig. 6 qualitatively shows the variation in the electrostatic potential distribution for these two cases. Based on the above arguments,  $(\phi^{\text{PET}} - \phi^{\text{S}})$  is expected to increase with increasing  $B$  or  $\omega$ , a consequence of the increase in the rate of which charge-compensating ion are transported out of the depletion layer. This prediction is consistent with the experimentally observed shift in  $E_{1/2}$  with increasing  $B$  or  $\omega$ .

Figs. 2 and 3 show that the overpotential is insignificant in 0.1 M TBAP solutions for all  $B$  or  $\omega$ , and large in 0.01 M TBAP solutions. In a previous study, we have shown that the ohmic overpotential at a RMDE is insignificant for solutions in which  $C_{\text{elec}}/C_{\text{redox}} > 0.1$ , but rapidly increases as  $C_{\text{elec}}/C_{\text{redox}}$  is decreased [28]. To our knowledge, no quantitative theoretical description of the dependence of  $(\phi^{\text{PET}} - \phi^{\text{S}})$  on  $C_{\text{elec}}/C_{\text{redox}}$  exists for the RMDE or a stationary electrode in a magnetic field. However, it is interesting to note that a qualitatively similar dependence of  $(\phi^{\text{PET}} - \phi^{\text{S}})$  on  $C_{\text{elec}}/C_{\text{redox}}$  is observed in the voltammetric response of both the RMDE and the stationary electrode in a uniform magnetic field. In each case, a significant shift in  $E_{1/2}$  is observed when  $C_{\text{elec}}/C_{\text{redox}} = 0.01$ , but not for  $C_{\text{elec}}/C_{\text{redox}} = 0.1$ . The similar dependency of  $E_{1/2}$  on  $C_{\text{elec}}/C_{\text{redox}}$  underscores the fact that the overpotential results from fluid convection in both cases.

**Dependence of Limiting Current Enhancement on Magnetic Force.** The dependence of the enhancement of  $i_{\text{lim}}$  on several experimental parameters is described in this section. Various correlations of the general form  $i_{\text{lim}} \propto B^x$  have been proposed in the literature, with  $x$  ranging from  $-0.25$  to  $1.6$  [1-13]. However, these correlations are for large electrodes where natural convection is the primary mode of steady-state transport in the absence of the magnetic field. In order to determine the critical factors that influence the magnitude of the magnetic field effect at microdisk electrodes, we have measured  $i_{\text{lim}}$  as a function of  $r_0$ ,  $B$ , and  $C_{\text{redox}}$  for five redox reactions. These correspond to the  $1\text{-e}^-$  reductions of NB, acetophenone (AP), and benzophenone (BP) in  $\text{CH}_3\text{CN}$  solutions, and the

oxidation/reduction of  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  in aqueous solutions. All solutions used in these experiments contained 0.1 to 0.2 M electrolyte ( $\text{TBAPF}_6$  in  $\text{CH}_3\text{CN}$  or  $\text{KCl}$  in  $\text{H}_2\text{O}$ ). Well-defined sigmodal-shaped voltammograms for each reaction are observed at 6.4  $\mu\text{m}$ -radius Au and 12.5 and 25  $\mu\text{m}$ -radius Pt microdisks. A magnetic field enhanced limiting current is also observed for each reaction, qualitatively similar to the results shown in Fig. 2 for NB reduction.

A general observation from our investigations is that the enhancement in the voltammetric current, defined here as  $i_B - i_0$  (where  $i_B$  and  $i_0$  are equal to  $i_{\text{lim}}$  with and without the magnetic field, respectively), is approximately proportional to both  $i_0$  and  $B$ , i.e.,  $i_B - i_0 \propto i_0 B$ . This finding is general for the five redox systems investigated. However, no specific correlation appears to exist between  $i_B - i_0$  and  $C_{\text{redox}}$ . For example, as noted for the NB system, the largest enhancement in voltammetric currents occurs at  $C_{\text{NB}} \sim 2.5$  M, becoming vanishingly small in solutions containing very low (1 mM) and very high (9.1 M) redox concentrations.

Fig. 7 shows a plot of  $i_B - i_0$  vs.  $i_0 B$  for the five redox species (NB, AP, BP,  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ). Measurements were made at a 25  $\mu\text{m}$ -radius Pt disk for field strengths ranging from 0.1 to 0.8 T (indicated on the figure), and for redox concentrations ranging from  $\sim 10$  mM to  $\sim 10$  M. Recognizing that the quantity  $i_0 B$  represents the force per unit length (N/m) directly at the electrode surface, the data in Fig. 7 suggest that current enhancement observed at microdisks increases linearly in proportion to the magnetic force acting on the depletion layer. A complete interpretation of this observation requires a detailed treatment of the fluid mechanics at the microdisk surface, and is beyond the scope of the present investigation.

Fig. 8 shows a plot of  $i_B - i_0$  vs.  $i_0 B$  for very small values of  $i_0 B$  (corresponding to experiments involving very low and high redox concentrations and low magnetic field strengths). All results obtained at 6.4, 12.5, and 25  $\mu\text{m}$ -radius microdisks for the 5 redox systems are included in this data set. Although there is significant scatter in the data, the figure clearly indicates that the plot of  $i_B - i_0$  vs.  $i_0 B$  has a non-zero intercept. This results suggests that a minimum value of magnetic force is necessary to observe an enhancement of the limiting current. Since the enhancement in current is due to convective fluid flow, the results also suggest, albeit indirectly, the existence of a threshold force necessary to induce flow across the microelectrode surface. We note that the force acting *directly* on the charge

carrying ions (e.g.,  $\text{NB}^-$  for NB reduction) remains finite for all finite values of  $i_0B$ . Thus, a minimum acceleration of ions may be required to induce solution flow. We are currently exploring this experimental observation in more detail.

**Conclusion.** Our investigations have demonstrated that the voltammetric response of a microdisk electrode can be controlled using an externally-applied, uniform magnetic field. Similar to previous observations made using macroscopic electrodes, molecular transport of both neutral and charged electroactive species is enhanced when the magnetic field is parallel to the electrode surface. The mechanism of the observed enhancement is consistent with acceleration of the current carrying ions by the magnetic field, resulting in convective solution flow. This conclusion is strongly supported by the observations that: (i) voltammetric currents for neutral species are enhanced by the magnetic field, and (ii) a general relationship (i.e., independent of the redox system) exists between the limiting current enhancement ( $i_{\text{lg}} - i_0$ ) and magnetic force ( $i_0B$ ).

We have established that the enhancement in current at a microdisk is proportional to the magnetic force, the latter quantity computed based on the current measured in the absence of the magnetic field and the field strength ( $i_0B$ ). In addition, we have obtained preliminary evidence of a critical threshold value of magnetic force necessary to engender convective solution flow at a microdisk. In this regard, microdisk voltammetry may be useful as a tool in investigations of fluid mechanics in ultrasmall volumes.

In addition to documenting an enhancement in molecular transport rates at microelectrodes, we have also shown that the interfacial potential and ion distribution are dependent on the magnetic field strength. Convective fluid flow resulting from the magnetic force removes the electrolyte counterions required to maintain local electroneutrality, analogous to the effect of electrode rotation. Consequently, in low ionic strength solutions ( $C_{\text{elec}}/C_{\text{redox}} < 0.1 \text{ M}$ ), the magnetic field reduces the driving force for electron transfer, resulting in a significant reaction overpotential.

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## Figure Captions

1. (Top) Experimental arrangement (view from above) for the measuring the voltammetric response of a microdisk electrode as a function of the magnetic field strength. (Bottom) Side view of the orientation of the microelectrode relative to the magnetic field ( $B$ ). The angle between net current ( $i$ ) and magnetic field is  $90^\circ$ . The current is directed inwards towards the electrode for an electrochemical reduction. The net magnetic force is directed out of the paper.
2. Voltammetric response of a  $25\text{ }\mu\text{m}$ -radius Pt microdisk electrode as a function of applied magnetic field strength ( $B$ ). The  $\text{CH}_3\text{CN}$  solution contained  $1\text{ M}$  NB and either (a)  $0.1\text{ M}$  TBAPF<sub>6</sub> or (b)  $0.01\text{ M}$  TBAPF<sub>6</sub>. Scan rate,  $5\text{ mV/s}$ .
3. Voltammetric response of a  $25\text{ }\mu\text{m}$ -radius Pt microdisk electrode as a function of angular velocity ( $\omega$ ). The  $\text{CH}_3\text{CN}$  solution contained  $1\text{ M}$  NB and either (a)  $0.1\text{ M}$  TBAPF<sub>6</sub> or (b)  $0.01\text{ M}$  TBAPF<sub>6</sub>. Scan rate,  $20\text{ mV/s}$ .
4. Schematic drawing of the direction and magnitude of the local magnetic force (indicated by arrows) within the depletion layer. The drawing corresponds to the electrochemical reduction of a neutral species. Lines originating on the electrode surface represent the diffusion-migration paths of electrochemically-generated anions. By convention, positive current flows into the surface for an electrochemical reduction. The direction of the magnetic force would be rotated by  $180^\circ$  for an electrochemical oxidation. (For clarity, the electrode is drawn facing upward; in the experiments, the electrode faces downward).
5. Schematic diagram of the ion distribution at: (a) a stationary microelectrode in the absence of a magnetic field, (b) a stationary electrode in the presence of a magnetic field; and (c) a rotated microelectrode. The solid lines are qualitative representations of the fluid streamlines resulting from the magnetic field and electrode rotation.
6. Schematic of the electrostatic potential distribution at a microdisk electrode in a low ionic strength solution. The drawings correspond to (a) finite current at a stationary

electrode in the absence of a magnetic field or electrode rotation; (b) finite current at either a rotated microdisk or a stationary disk in the presence of a magnetic field.

7. Plot of enhancement in voltammetric current  $|i_B - i_0|$  at a 25  $\mu\text{m}$ -radius Pt electrode as a function of the magnetic force per unit length,  $i_0 B$ . The data correspond to measurements using five redox-active species (nitrobenzene, 0.05 - 4 M; acetophenone, 0.05 - 8.6 M; benzophenone, 0.2 - 4 M; ferricyanide, 0.5 M; and ferrocyanide, 0.5 M). Supporting electrolyte concentration: 0.1 - 0.2 M.
8. Plot of enhancement in voltammetric current  $|i_B - i_0|$  at 6.4, 12.5 and 25  $\mu\text{m}$ -radius microdisk electrodes as a function of the magnetic force per unit length,  $i_0 B$ . Solution conditions are the same as in Fig. 7.

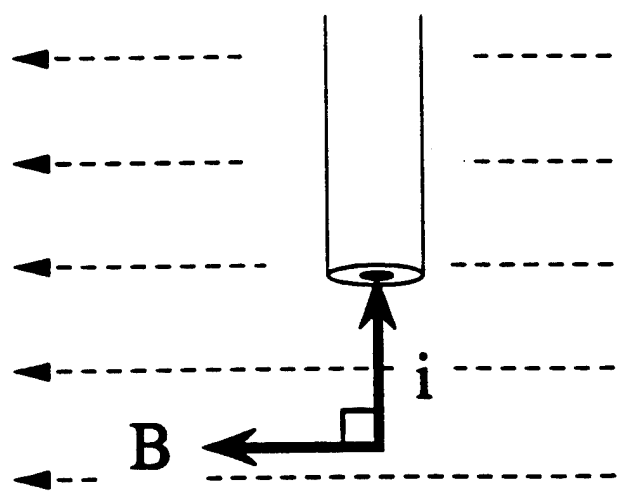
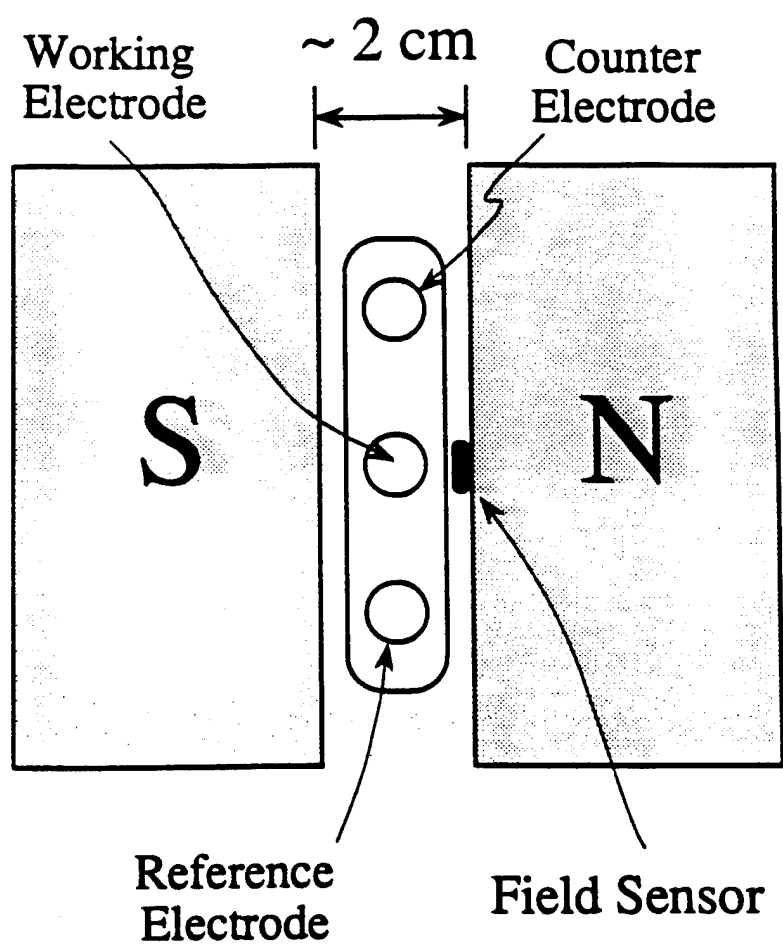
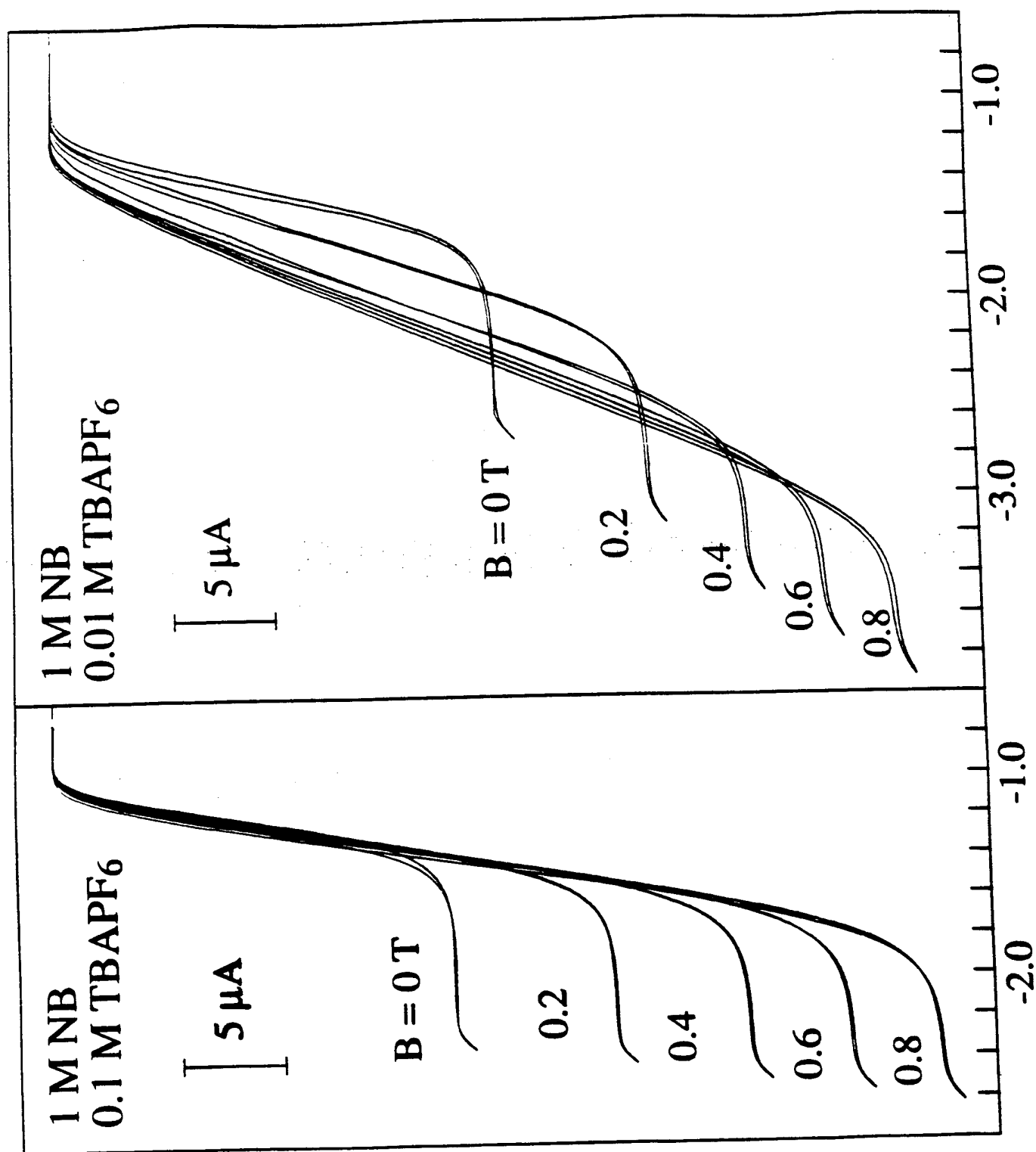


Fig. 1



V vs.  $\text{Ag}/\text{Ag}_x\text{O}$

Fig. 2

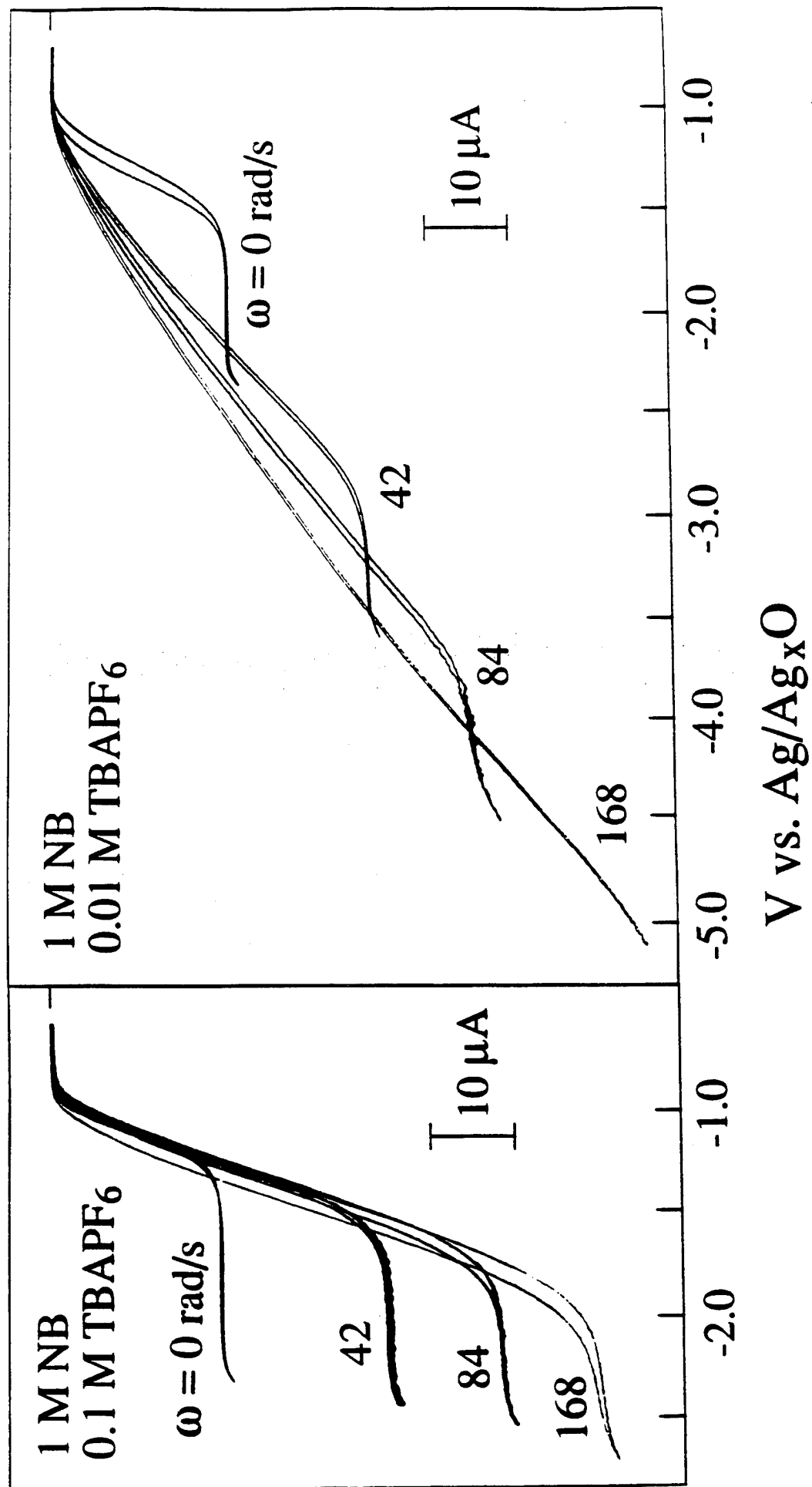


Fig. 3

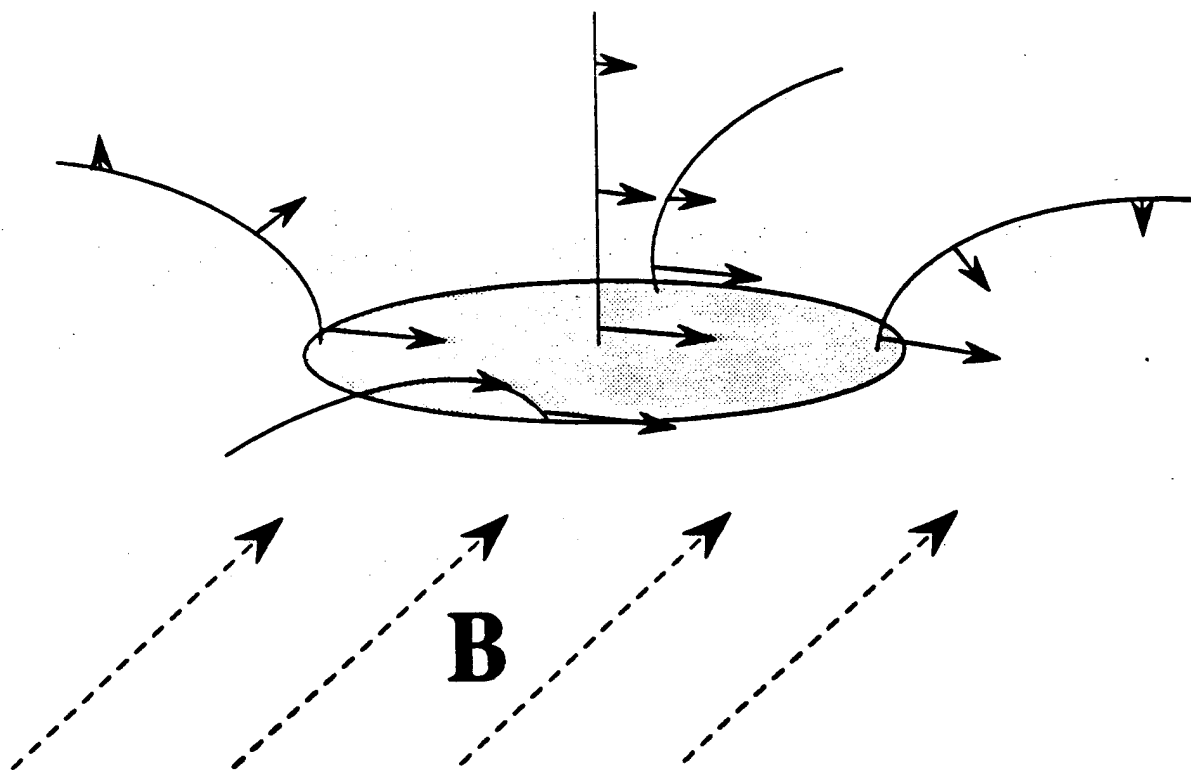
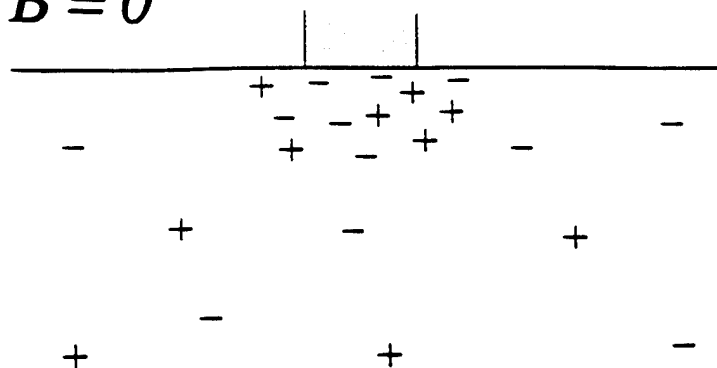


Fig. 4

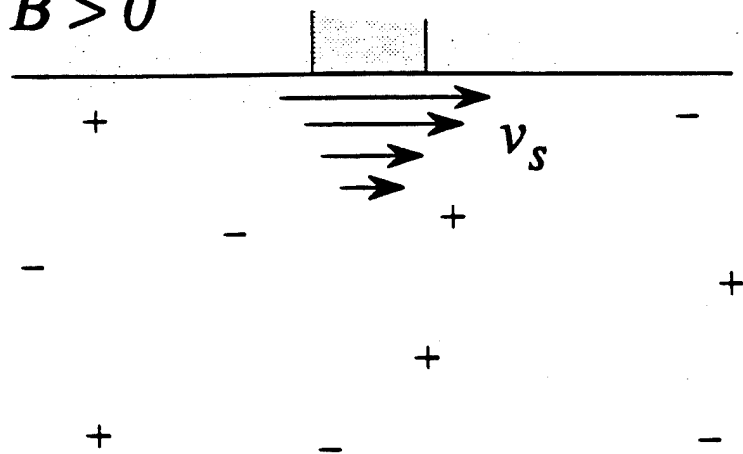


(A)  $\omega = 0$

$B = 0$



(B)  $B > 0$



(C)  $\omega > 0$

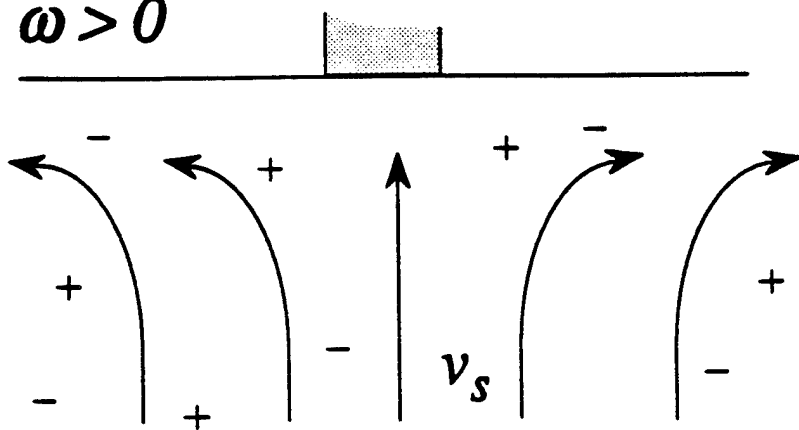
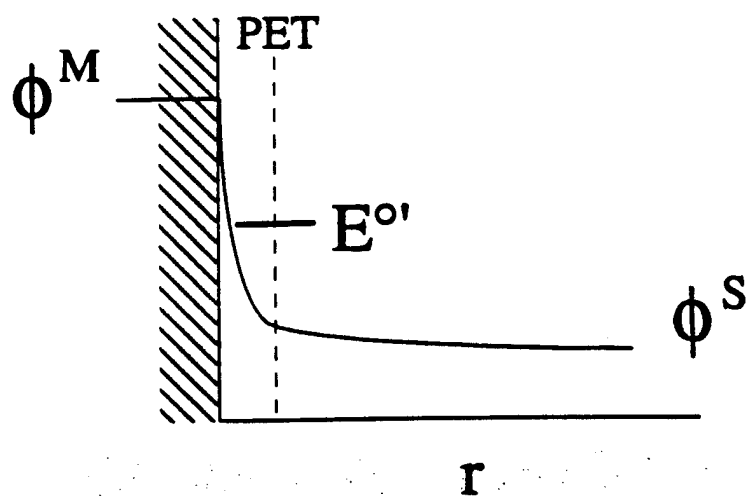


Fig. 5

(A)



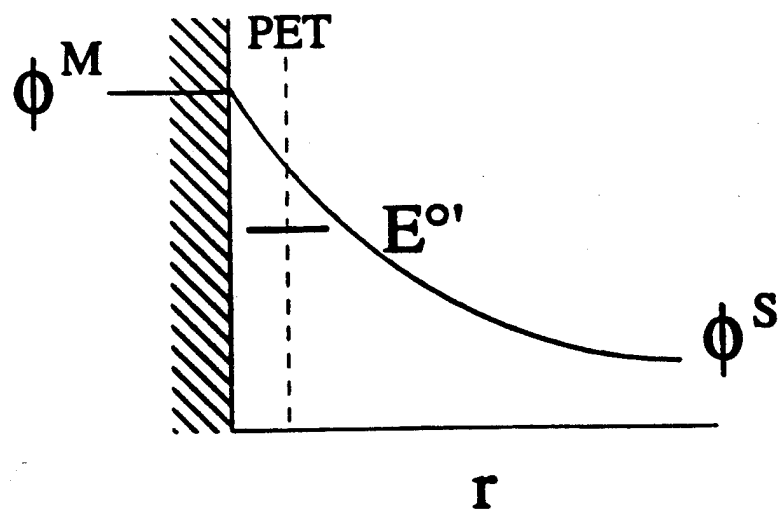
\*  $|i| > 0$

\*  $\omega = 0$

and

$B = 0$

(B)



\*  $|i| > 0$

\*  $\omega > 0$

or

$B > 0$

Fig. 6

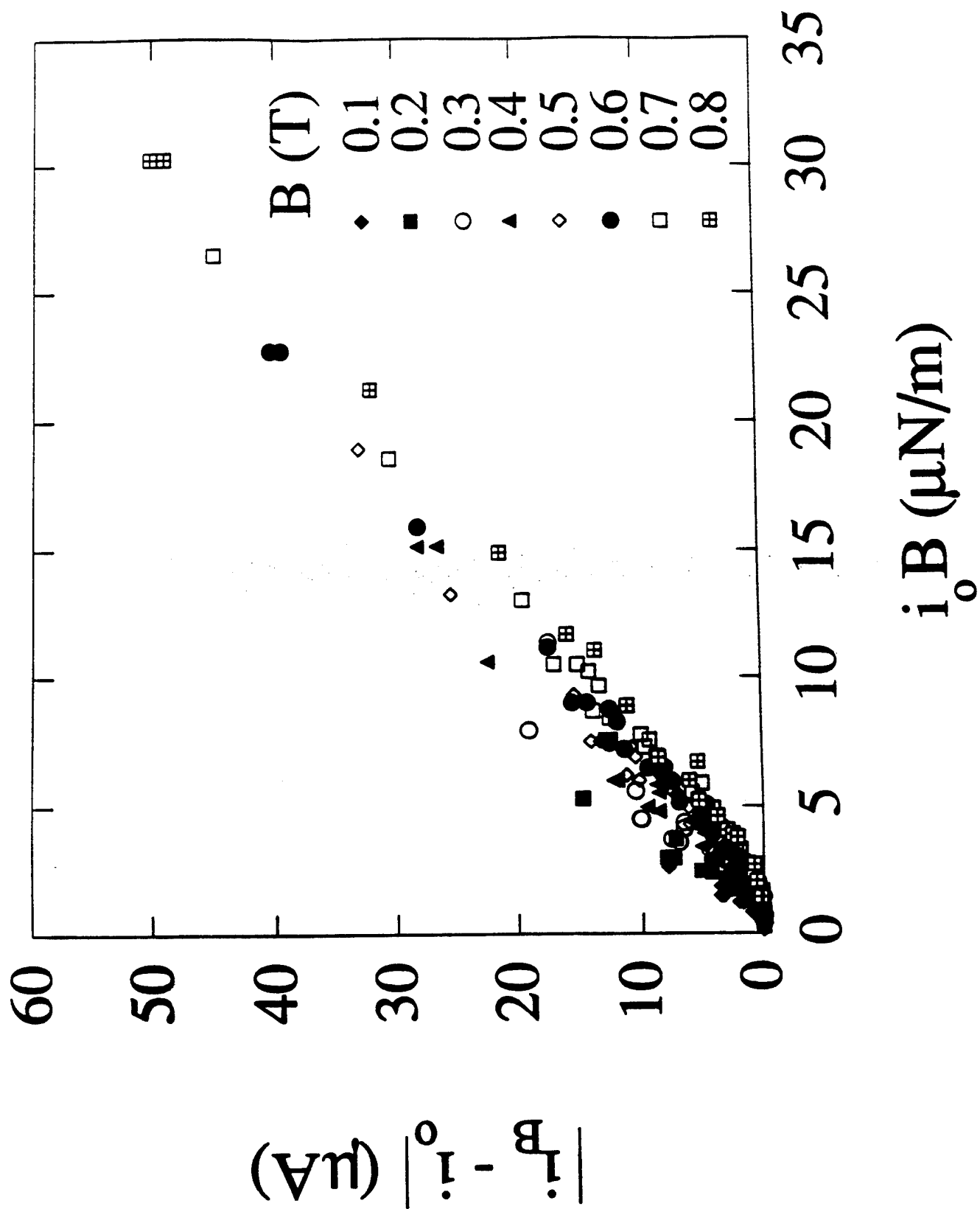


Fig.7

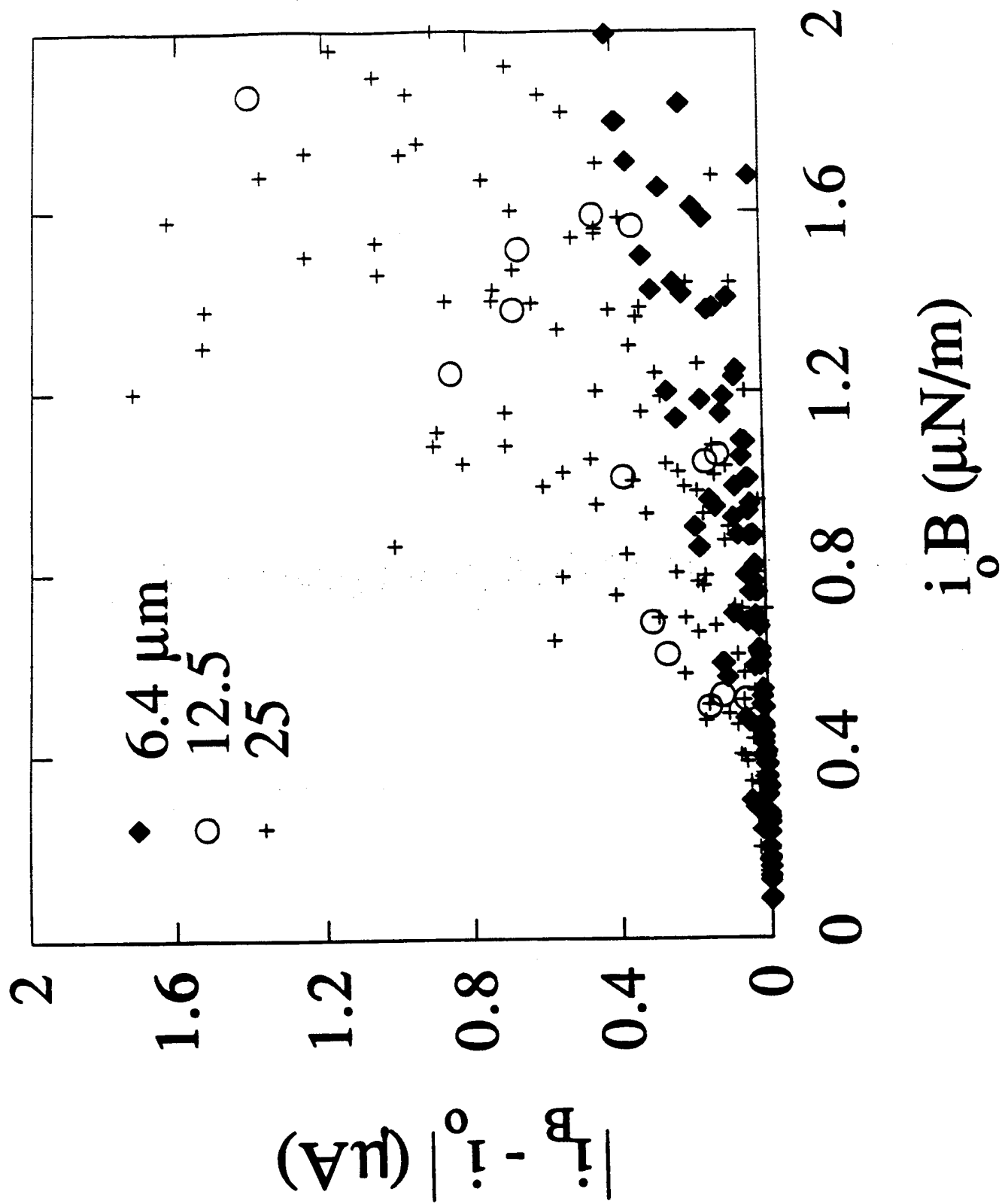


Fig. 8